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Assessment of aided phytostabilization of copper-contaminated soil by X-ray absorption spectroscopy and chemical extractions

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Soil treatment with compost and iron grit caused a shift in predominant Cu forms from non-specifically bound Cu ions to Cu species bound to Fe oxyhydroxides.

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ABSTRACT

Field plots were established at a timber treatment site to evaluate remediation of Cu contaminated topsoils with aided phytostabilization. Soil containing 2600 mg kg⁻¹ Cu was amended with a combination of 5 wt% compost and 2 wt% iron grit, and vegetated. Sequential extraction was combined with extended X-ray absorption fine structure (EXAFS) spectroscopy to correlate changes in Cu distribution across five fractions with changes in the predominant Cu compounds two years after treatment in parallel treated and untreated field plots. Exchangeable Cu dominated untreated soil, most likely as Cu(II) species non-specifically bound to natural organic matter. The EXAFS spectroscopic results are consistent with the sequential extraction results, which show a major shift in Cu distribution as a result of soil treatment to the fraction bound to poorly crystalline Fe oxyhydroxides forming binuclear inner-sphere complexes.

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1. Introduction

Aided phytostabilization involves combining soil amendments with contaminant-tolerant plants to remediate polluted land. Numerous laboratory and field experiments have explored the efficacy of this remediation strategy (e.g. Knox et al., 2001; Kumpiene et al., 2008; Mench et al., 2000a; Vangronsveld et al., 1995). Main issues usually considered are the efficiency of soil amendments to reduce trace element mobility, sustain vegetation growth and facilitate the overall recovery of soil function. The long-term stability of immobilized trace elements in soils undergoing aided phytostabilization has been predicted for various environmental scenarios by conducting simple leaching tests and more detailed sequential extractions (Hanc et al., 2009; Hartley et al., 2009; Lombi et al., 2002), geochemical modeling to identify mineral phases of known solubilities (Cao et al., 2009; Kumpiene et al., 2007), and in relatively fewer studies by direct soil analysis using advanced spectroscopic techniques (Gardea-Torresdey et al.,

2005; Manceau et al., 2008; Nachtegaal et al., 2005; Panfili et al., 2005). Knowing what kind of compounds and molecular bonds prevail between trace elements and soil constituents, allows prediction of the possible fate of the immobilized elements in soil. For example, identification of stable mineral phases, such as pyromorphite-like structures in bulk soil containing Pb (Cotter-Howells et al., 1994), is an evidence of successful Pb immobilization in soil. This collective body of research demonstrates the need for a combination of various techniques to provide a comprehensive picture of the treated soil condition.

Wood preservation industry is a common source of soil pollution with various chemicals used in wood treatment processes around the world. Arsenic, copper, chromium, zinc and polycyclic aromatic hydrocarbons derived from creosote are common soil contaminants found in such sites often requiring immediate remediation. Aided phytostabilization has been studied as an option for remediating a wood preservation site contaminated with Cu in Saint Médard d'Eyrans, France. Thirteen organic and inorganic soil amendments were tested for their ability to reduce the mobile Cu fraction in soil and its accumulation in plants (Bes and Mench, 2008). A combination of 5 wt% compost produced from poultry manure and pine bark chips (C) and 2 wt% zerovalent iron grit (ZVI) showed one of the best results in reducing Cu solubility in soil.

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Although this treatment was less efficient in reducing Cu concentration in soil solution than activated carbon and zerovalent iron alone or their combination, it was more successful in promoting plant biomass production and decreasing oxidative stress (Bes and Mench, 2008). Additional analysis methods are needed to determine how Cu is immobilized as a result of soil treatment at the site. Synchrotron based X-ray absorption spectroscopic (XAS) techniques are analytical methods that can be used to determine the coordination chemistry of trace elements in bulk soil samples (Manceau et al., 2000; Gardea-Torresdey et al., 2005). These methods do not require sample pretreatment or drying, and therefore are an ideal complement to chemical extractions or other indirect soil analysis methods.

This study aimed at comparing the dominant Cu forms present in contaminated soil with those present in soil remediated by aided phytostabilization for predicting the long term efficiency of the soil treatment. Extended X-ray absorption fine structure (EXAFS) spectroscopy, in combination with sequential extraction, were applied to samples collected two years after soil treatment in field experiments.

2. Materials and methods

2.1. Soil and amendments

Field plots (3 m × 6 m) were established in 2006 at a wood preservation site in Saint Médard d'Eyrans, France, for remediation of Cu contaminated topsoils by aided phytostabilization. Soil, initially containing 2600 mg Cu kg⁻¹ and 2.7% organic matter, was amended with a combination of 5 wt% compost (C) produced from poultry manure and pine bark chips and 2 wt% zerovalent iron grit (ZVI). The compost from Orisol, Cestas, France, contained (in g kg⁻¹) organic carbon 321, CaO 47, P₂O₅ 18, K₂O 11, SO₃ 4.9, MgO 4.7, Na₂O 1.4, and (in mg kg⁻¹) Zn 131, Cu 32.1, Pb 9.0, Ni 1.8, Cd 0.5 (Bes and Mench, 2008). Zerovalent iron grit (GH120, particle size < 0.1 mm) was composed of metallic iron (97%) and impurities such as Mn (0.8%), Cr (0.3%), Cu (0.1%), Ni, Al (<0.1%) (Mench et al., 2000b). Poplar, willows and grasses were transplanted in both untreated and C-ZVI-treated plots in 2006.

Soil samples from parallel plots of untreated and treated soil were collected two years later from 0–25 cm topsoil layer using a stainless steel spade. Soil attached to the roots (rhizosphere soil) was excluded. Four soil sub-samples collected on a circle of 2 m-diameter from each plot were combined into one composite sample. These samples were air dried, homogenized and sieved <2 mm. The mass reduction to the required sub-sample size was done by fractional shoveling (Petersen et al., 2005) prior to analyzing for total element composition, total and organic carbon content, pH, electrical conductivity, sequential extractions and EXAFS spectroscopy.

For determining the elemental composition, 1 g of soil was digested in 15 mL aqua regia at 195 °C for 10 min using a microwave digester (CEM Microwave Sample Preparation System, Model MARS 5) and analyzed with ICP-OES (Optima 2000DV, Perkin Elmer). Total carbon (TC) and total organic carbon (TOC) of the bulk soil were determined using a TOC analyzer (TOC-VCPH/CPN Shimadzu Corporation). For determining TC, the samples were oxidized at 900 °C and the formed CO₂ was analyzed by non-dispersive infrared absorbance (NDIR). For TOC quantification, the samples were pre-treated with concentrated HCl to remove the inorganic carbon (IC) and analyzed with NDIR as described above. Soil pH and electrical conductivity (EC) were measured in 1:2 soil-double distilled water suspensions after one hour equilibration time.

2.2. Plant analyses

Plants growing on the treated plot at the sampling time (two years later) were *Agrostis capillaris* L., *Agrostis castellana* Boiss. & Reut., *Agrostis gigantea* Roth., *Dactylis glomerata* L., *Holcus lanatus* L., *Populus nigra* L., *Salix caprea* L. and *Salix viminalis* L. The untreated plot contained only *A. castellana* patches. Shoots were collected together with soil sampling, washed with distilled water, dried at 65 °C and ground. 0.5 g DW of plant material was wet-digested with 5 mL 14 M HNO₃, 2 mL 30% H₂O₂ and 1 mL distilled water using a CEM MarsXpress microwave digester. Digests were made up to 100 mL with distilled water. Certified reference material (BIPEA maize V463) was included in each series. Element composition in digests was determined by ICP-AES (Varian Liberty 200). Copper recovery was within the limits defined by the standard deviation of the certified value.

2.3. Sequential extraction of Cu

Extraction of Cu associated with five operationally defined fractions was performed in triplicate as follows:

- (1) Exchangeable fraction: 1 M NH₄-acetate pH 4.5 at liquid to solid ratio (L/S) 25, shaking for 2 h at room temperature (RT), followed by centrifugation at 1200 g for 15 min and rinsing with 10 mL of deionised water (centrifuged and discarded) (Dold, 2003).
- (2) Fe(III) oxyhydroxides: 0.2 M NH₄-oxalate pH 3.0, L/S 25, shaking for 2 h at RT in darkness, centrifugation at 1200 g for 15 min (Dold, 2003). Extraction time was increased from 1 (as suggested by Dold, 2003) to 2 hours to obtain more complete dissolution of ferrihydrite (Cornell and Schwertmann, 2003). The washing step was adopted from Wenzel et al. (2001), i.e., the same NH₄-oxalate solution was used at L/S 12.5 and, after centrifugation and filtration, was combined with the previously extracted portion (making in total L/S 37.5). The step was finished by rinsing with 10 mL of deionised water (centrifuged and discarded).

Other soil constituents, such as amorphous Mn and Al oxides, can also get solubilised during this extraction step. It was assumed here that Mn had negligible impact on Cu sorption in the treated soil due to the relatively low total concentration compared to Fe concentration (Table 1), while Al content remained unaltered in both soils and the amount of Cu erroneously assigned as sorbed to Fe(III) oxyhydroxides is expected to be of the same magnitude in both samples.

- (3) Fe–Mn oxides: 0.04 M NH₂OH-HCl in 25% (v/v) HO-acetate pH 2, L/S 20, heated in water bath at 96 °C for 6 h, centrifugation at 13 000 g for 30 min, rinsing with 10 mL deionised water (centrifuged and discarded) (Tessier et al., 1979).
- (4) Organic matter and secondary sulfides: 35% H₂O₂, heated in water bath at 85 °C for 2 h, L/S 25, centrifugation at 1200 g for 15 min, rinsing with 10 mL of deionised water (centrifuged and discarded) (Dold, 2003).
- (5) Residual fraction: aqua regia (HNO₃:HCl, 1:3 v/v), L/S 15, in a microwave digester (CEM Microwave Sample Preparation System, Model MARS 5) at 195 °C for 10 min.

All extracts were filtered through 0.45 µm cellulose acetate syringe filters and stored at 4 °C prior to analyses by ICP-OES (Optima 2000DV, Perkin Elmer). The limit of detection for Cu was 2 µg L⁻¹ and the limit of quantification was 7 µg L⁻¹. The measured Cu concentrations deviated from the concentrations in quality control solutions by 3–10%.

2.4. EXAFS analyses

2.4.1. Data collection

Extended X-ray absorption fine structure spectroscopy (EXAFS) analyses were performed using beamline X11-A at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY. Air-dried soil samples were packed into Teflon holders between polypropylene windows, and mounted at 45° to the incident beam. A Ni filter (thickness of 6 adsorption lengths) was placed between the sample

Table 1

Selected properties of untreated soil and soil treated with poultry manure compost (C) and zerovalent iron grit (ZVI) two years after the start of the aided phytostabilization experiment ($n = 3$, \pm sd).

Element	Untreated soil	C-ZVI treated soil
pH	6.21 ± 0.01	7.00 ± 0.02
Electrical conductivity (EC, µS cm ⁻¹)	19.3 ± 1.9	16.3 ± 2.1
Total carbon (TC, %)	1.57 ± 0.35	2.76 ± 0.20 ^a
Organic carbon (OC, %)	1.51 ± 0.05	1.92 ± 0.37
<i>Elements (mg kg⁻¹ dw)</i>		
Al	12,486 ± 1641	11,302 ± 110
As	16.9 ± 4.9	12.3 ± 1.6
Ca	1077 ± 158	2470 ± 191
Cd	<0.01	<0.01
Cr	22.8 ± 2.8	90.5 ± 8.3 ^a
Cu ^b	2080 ± 14	1264 ± 43 ^a
Fe	10,593 ± 1679	30,219 ± 2450 ^a
K	1911 ± 183	1553 ± 77 ^a
Mg	1025 ± 142	985 ± 26
Mn	159 ± 12	398 ± 18 ^a
Mo	<0.09	5.1 ± 0.6 ^a
Na	340 ± 44	310 ± 38
Ni	8.7 ± 1.1	41.1 ± 3.3 ^a
Pb	35.9 ± 2.0	29.9 ± 3.3
Zn	78.0 ± 10.6	61.4 ± 2.2
S	243 ± 15	285 ± 17 ^a

^a Statistically significant difference between treated and untreated sample at 95% confidence level.

^b Calculated from sequential extraction results.

and the detector to reduce the fluorescence background. The spectrum of a metallic Cu foil was collected in the transmission mode for the reference of the edge position. Spectra of 11–12 scans per sample were collected at room temperature in fluorescence mode with a 13-element Ge solid-state detector and a Si(111) double crystal monochromator. EXAFS data were collected in the X-ray energy range between 8779 and 9954.3 eV with the Cu K-edge calibrated to 8979 eV. In total 463 points per scan with an exposure time of 3 s per point were collected in three X-ray energy intervals: 10 eV steps from 200 eV to 50 eV before the edge; 0.5 eV steps from 50 eV before to 50 eV after the edge; and 50 eV steps from 50 eV to 1600 eV after the edge.

2.4.2. Data analysis

The collected XANES data were processed using Athena software (Ravel, 2008) including data normalization based on the Cromer-Lieberman calculations, background removal using the AUTOBK algorithm, alignment and merge of scans. The processed EXAFS spectra were saved as $\chi(k)$ and fitted with the theoretical models generated by FEFF7 using Artemis software. Data fitting was performed in k -space using k^3 -weighting factor, Hanning window function and k range interval 2–9 Å⁻¹. The fitting was done by allowing the edge energy (ΔE_0) to float, but restraining between the shells. The coordination number (CN) of the first shell was set to 4 and for the higher shells was allowed to float. The Debye–Waller factor (σ^2) for the Cu–O shell was set to 0.005 Å² and for the higher shells of the untreated soil was set to 0.01 Å². Distances to neighboring atoms (Δr) were allowed to vary throughout the fits. The global amplitude reduction factor (S_0^2) was fixed at 0.7 after Fitts et al. (1999), which is based on fitting model compounds of Cu(II)-glutamate, Cu(OH)₂, and aquo-Cu(II) ions using phase and amplitude functions generated by FEFF7. Models with one shell, two shells with single scattering and three shells with multiple scattering were tested to fit the experimental data. In all cases, the possible presence of C, Cu, Fe and Al in second and higher shells was examined. The best fits were obtained by introducing multiple scattering paths into the models. The statistical significance of including additional shells was evaluated based on the method reported by Fitts et al. (2000).

3. Results

3.1. Soil properties

Soil treatment with compost and iron grit resulted in neutralized soil pH (from 6.2 to 7.0), increased total carbon, and changes in the concentrations of several elements (Table 1). The concentrations of Fe, Cr, Mn, Ni and Mo increased due to the presence of these elements in the iron grit, while higher S amount originated from the compost. Except for Cu, none of the elements exceeded the guideline values for soils at industrial sites (SEPA, 2008).

3.2. Plant establishment and accumulation of elements

Although all trees and grasses were transplanted in both untreated and C-ZVI-treated plots, their establishment differed considerably. All plant species developed on C-ZVI soil, whereas only the metal-tolerant *A. castellana* survived on untreated soil.

Copper concentration in foliar tree parts and grass shoots of transplanted plants collected two years after the experiment start was 274.5 ± 1.1 mg kg⁻¹ dw in the untreated soil and in total 275.8 ± 56.2 mg kg⁻¹ dw in the treated soil (Table 2). Soil treatment

Table 2
Foliar (for trees) and shoot (for grassy plant species) Cu concentrations of transplanted plants collected two years from the start of the experiment ($n = 3$, \pm sd).

Plot	Plant species	Cu mg kg ⁻¹ dw
C-ZVI-treated soil	<i>Agrostis capillaris</i> L.	54.6 ± 11.3
	<i>Agrostis castellana</i> Boiss. & Reut.	70.1 ± 31.7
	<i>Agrostis gigantea</i> Roth.	37.3 ± 22.1
	<i>Dactylis glomerata</i> L.	51.4 ± 38.8
	<i>Holcus lanatus</i> L.	15.9 ± 0.3
	<i>Populus nigra</i> L.	16.2 ± 1.4
	<i>Salix caprea</i> L.	18.3 ± 4.3
	<i>Salix viminalis</i> L.	12.0 ± 2.7
	Total	275.8 ± 56.2
Untreated soil	<i>Agrostis castellana</i> Boiss. & Reut.	274.5 ± 1.1

decreased Cu concentration in shoots of *A. castellana* four times compared with the plants grown in untreated soil. Since only one plant species survived in untreated soil, the analysis of the impact of soil treatment on Cu concentration in other plants was not possible.

3.3. Cu fractionation in soil

Sequential extractions were performed to determine the Cu distribution between five operationally defined soil fractions (Fig. 1). In the untreated soil, the dominant Cu fraction was exchangeable (1235 ± 14 mg kg⁻¹), which accounted for $59.4 \pm 0.7\%$ of total Cu (Fig. 1). The second most abundant fractions were bound to poorly crystalline Fe oxyhydroxides (445 ± 27 mg kg⁻¹ or $21.4 \pm 1.3\%$) and crystalline Fe–Mn oxides (272 ± 3 mg kg⁻¹ or $13.1 \pm 0.1\%$). Residual Cu (59 ± 9 mg kg⁻¹ or $2.8 \pm 0.4\%$) and that bound to organic matter (69 ± 3 mg kg⁻¹ or $3.3 \pm 0.2\%$) were the smallest fractions in the untreated soil.

Aided phytostabilization treatment caused a significant redistribution of Cu in the soil. The Cu fraction bound to poorly crystalline Fe oxyhydroxides became the largest fraction (626 ± 95 mg kg⁻¹ or $50 \pm 7\%$), as the amount of Cu in the exchangeable fraction (376 ± 20 mg kg⁻¹ or $30 \pm 2\%$) decreased significantly (Fig. 1). The concentration of crystalline Fe–Mn bound Cu decreased 3.5 times (from 272 ± 3 mg kg⁻¹ in the untreated soil to 77 ± 2 mg kg⁻¹ in C-ZVI treated soil), while OM-bound Cu significantly increased after treatment (from 69 ± 3 mg kg⁻¹ to 135 ± 7 mg kg⁻¹) and accounted for $11 \pm 1\%$ of the total Cu (Fig. 1). The residual fraction was the smallest and composed $3.9 \pm 0.4\%$ (50 ± 5 mg kg⁻¹) of the total soil Cu.

3.4. Cu K edge EXAFS analyses

The coordination chemistry of Cu was studied by EXAFS spectroscopy in subsamples of the untreated and stabilized soils collected two years after the treatment and subjected to the extraction studies described above. Ab initio model fits of the EXAFS spectra were used to identify differences in the distribution of Cu species in these untreated and treated soils analyzed in parallel. All spectra were consistent with divalent Cu species, as was expected given the constant oxic conditions in both treated and untreated plots. Furthermore, evidence of X-ray beam induced reduction to monovalent or zerovalent Cu was not observed in the first derivative of the XANES spectra (Strawn and Baker, 2009). Fig. 2 shows EXAFS normalized k^3 -weighted χ spectra and Fourier transforms (FT) for Cu in untreated and C-ZVI treated soils and the

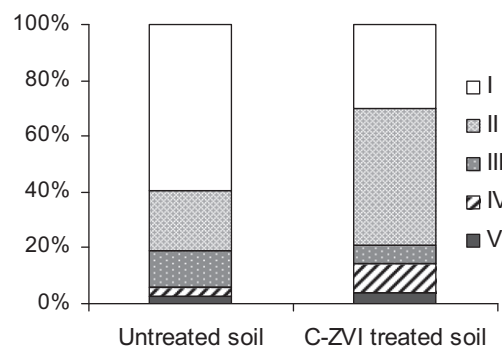


Fig. 1. Relative (%) fractionation of Cu between five fractions of untreated soil and soil treated with compost (C) and zerovalent iron grit (ZVI): I-exchangeable; II-bound to poorly crystalline Fe oxyhydroxides; III-bound to crystalline Fe–Mn oxides; IV-bound to organic matter; V-residual. Relative standard deviation for the fractions was 0.1–1.5% except for the fraction II in C-ZVI treated soil, which was 7%.

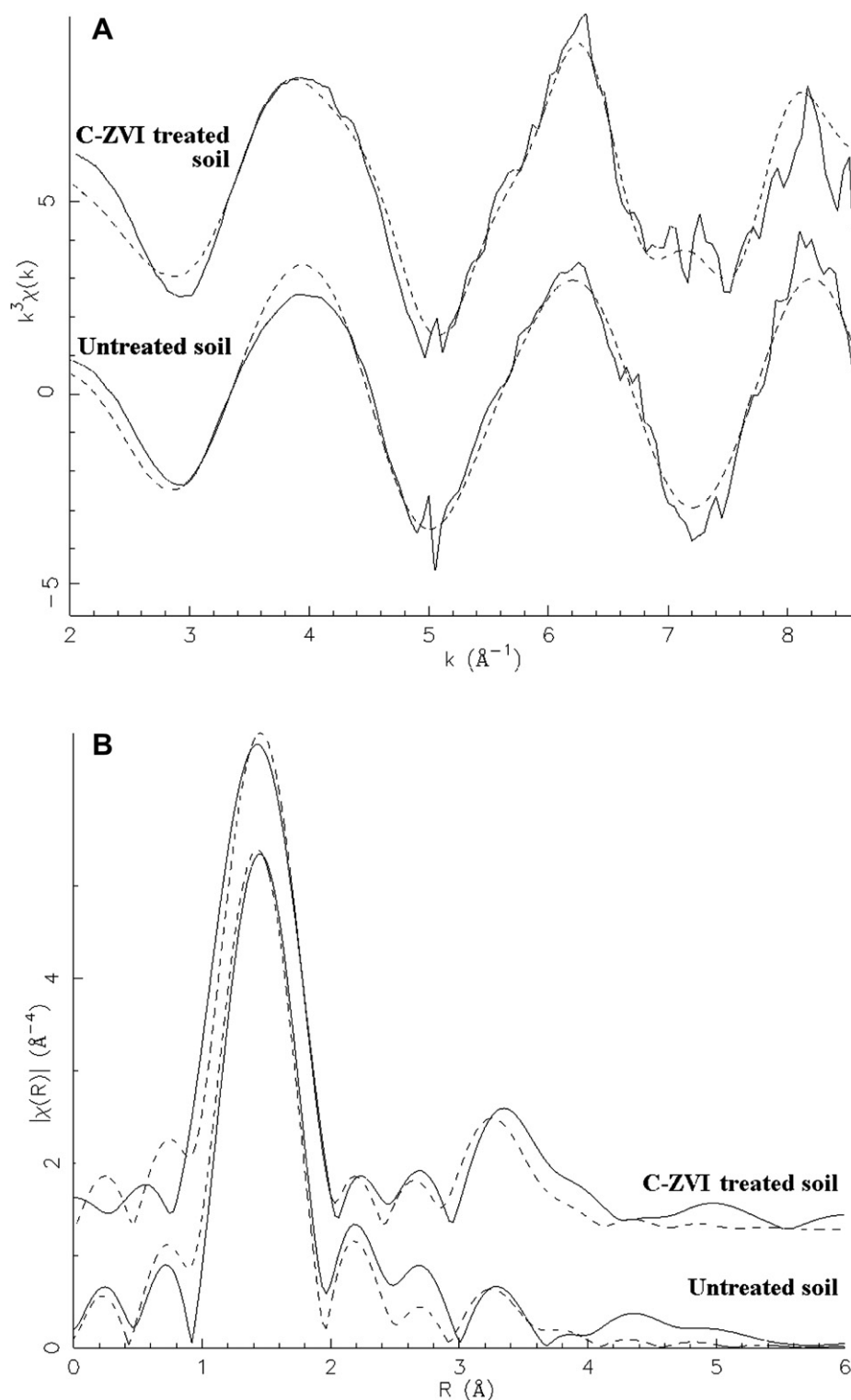


Fig. 2. A) EXAFS k^3 -weighted χ spectra and B) Fourier transforms (not corrected for phase shifts) for Cu in untreated and C-ZVI treated soil. Theoretical fits are signified by dashed lines.

corresponding best fits of each spectrum. Table 3 summarizes the fit results of the EXAFS spectra in k -space.

3.4.1. Untreated soil

The exchangeable fraction is presumed to represent non-specifically bound Cu, which is often referred to as electrostatic or outer-sphere binding. Therefore, the EXAFS spectrum of the

untreated soil was initially fit assuming a divalent Cu ion, where the octahedral coordination is distorted such that the Cu ion is surrounded by four equatorial and two axial water molecules at longer distances. In this configuration scattering from the two axial waters, which are at different distances, destructively interfere and as a result do not make an observable contribution to the EXAFS spectrum (Alcacio et al., 2001). The first peak in the FT of the

Table 3

Fitting parameters of EXAFS data for Cu(II) in untreated soil and soil amended with compost and zerovalent iron grit (C-ZVI). The amplitude reduction factor (S_0^2) was fixed at 0.7.

Atomic backscatter	R (Å)	CN	σ^2 (Å ²)	Goodness of fit (%)	ΔE_0 (eV)
<i>Untreated soil</i>					
Cu–O	1.96(±0.02)	4 ^f	0.005 ^f	1.8	–5.38
Cu–C	2.80(±0.13)	1.9(±1.4)	0.01 ^f	1.3	(±3.7)
Cu–O/C	3.84(±0.21)	2.1(±2.4)	0.01 ^f		
Cu–MS	4.24(±0.32)	1.8(±3.1)	0.01 ^f	1.1	
<i>C-ZVI treated soil</i>					
Cu–O	1.97(±0.02)	4 ^f	0.0057 ^f	11.2	–3.73
Cu–Cu	3.00(±0.19)	0.9(±1.9)	0.017(±0.02)	11.0	(±3.6)
Cu–Fe	3.18(±0.11)	1.8(±1.9)	0.017(±0.02)	10.3	
Cu–MS	3.79(±0.06)	3.6(±1.9)	0.017(±0.02)	7.7	

^f – fixed during the fitting. MS – multiple scattering; R – bond distance; CN – coordination number; σ^2 – Debye–Waller factor; ΔE_0 – edge energy.

untreated soil indicates an average inter-atomic distance of 1.96 (±0.02) Å to 4 equatorial oxygen atoms of the first hydration shell. The first-shell coordination environment of Cu(II) with 4 equatorial oxygen atoms was found to be around 1.85–2.05 Å and considered to be consistent with the protonated square-planar (CuO₄H_n)_n^{–6} ion (Peacock and Sherman, 2004). The Cu–O distance is consistent with the reported equatorial oxygen distances in soils (Strawn and Baker, 2009). Attempts to add a second shell with Fe or Cu shells failed to improve the fit and did not produce meaningful fit parameters. Evidence of backscattering from a second shell of Cu atoms, which would indicate the presence of a Cu dimer structure characteristic of CuO and Cu(OH)₂ precipitates (Peacock and Sherman, 2004), was not observed in attempts to fit a shell of Cu atoms at the characteristic distance of 2.9–3.0 Å.

Further attempts to fit the scattering observed beyond the first shell of equatorial oxygen atoms were made by adopting the model developed by Strawn and Baker (2008) for Cu(II) complexed by soil humic acids. The addition of organic complexation shells (Cu–C, Cu–O/C) and a multiple scattering path produced a statistically significant improvement ($R = 1.3\%$ and 1.1% , respectively) relative to the fit with a single Cu–Oeq shell ($R = 1.8\%$). This fitting approach produced Cu–C at 2.80(±0.13) Å, Cu–O/C at 3.84(±0.21) Å and Cu–C–O/C at 4.24(±0.32) Å. Karlsson et al. (2006) modeled Cu binding in various natural organic matter samples using a similar molecular structure where Cu(II) forms five-member chelate rings with O/N and C atoms. The ranges of distances observed by these authors for the nearest three shells were Cu–O 1.92–1.95 Å, Cu–C 2.76–2.86 Å, Cu–O/C 3.67–3.71 Å and Cu–C–O/C 4.14–4.24 Å. The distances reported by Strawn and Baker (2008) were Cu–O 1.94 Å, Cu–C 2.79 Å, Cu–O/C 3.72 Å and Cu–C–O/C 4.16 Å. Our fit results (Table 3) conform quite well with the reported atomic distances for Cu bound to both solid and dissolved organic matter.

3.4.2. Soil amended with compost and zerovalent iron grit

The average Cu(II) species in the treated soil was fit with a first atomic shell coordination environment of 4 equatorial O atoms at 1.97(±0.02) Å. In contrast to the untreated soil, the EXAFS spectrum of the treated soil shows evidence of higher frequency scattering ($k \sim 7.2 \text{ Å}^{-1}$) by ordered atomic shells beyond the equatorial oxygen atoms. The Cu–C–O/C structural model built for the untreated soil failed to fit these higher coordination shells. Given that the soil was amended with 2% metallic iron and the extraction results show a significant increase in the Cu fraction bound to Fe oxyhydroxides, a shell of Fe atoms was added assuming the previously reported edge-sharing Fe(O,OH)₆ polyhedra model of Cu(II) adsorbed on Fe oxyhydroxides (Peacock and Sherman, 2004). The model also includes Cu(II) dimers (Cu₂O₆H_n)_n^{–8} with a Cu–Cu distance of 3.00

(±0.19) Å and a Cu–Fe shell at 3.18(±0.19) Å, which is consistent with the Cu(II) adsorption as binuclear inner-sphere complexes to the Fe(hydr)oxide surfaces described by Peacock and Sherman (2004). The best fit was achieved by including all three scattering paths with a significant multiple scattering contribution (Table 3).

The second and higher coordination shells were also fit assuming only Cu atoms are present in order to identify Cu(OH)₂ precipitates in soil. The presence of Cu–Cu coordination is characteristic for Cu oxides and hydroxides with the intermetallic distances varying around 2.95–2.96 Å (Fitts et al., 1999; Oswald et al., 1990). However, Cu(OH)₂ precipitates should also show scattering from the four Cu atoms at the Cu–Cu distance of about 3.35 Å (Oswald et al., 1990; Fitts et al., 1999). Evidence for such a structure was not identified in our EXAFS data. Therefore, the EXAFS fit results for the treated soil indicate that the most significant fraction of Cu present within an ordered coordination environment is specifically bound to Fe oxyhydroxides forming binuclear inner-sphere complexes between Cu(II) dimers and Fe (O,OH)₆ polyhedra.

4. Discussion

4.1. Cu redistribution and mobility in C-ZVI treated soil

Aided phytostabilization using C-ZVI amendments has significantly reduced the fraction of exchangeable Cu two years after treatment, which is advantageous seeing as this Cu fraction is expected to be available for leaching and uptake by living organisms (Du Laing, 2010 and references within). Decrease in exchangeable Cu in the C-ZVI treated soil (Fig. 1) was well reflected by higher survival rate and growth of transplanted plant species in this plot, and decrease in shoot Cu concentration of *A. castellana* (Table 2). This decrease, however, can occur not only through Cu sorption by soil constituents such as Fe oxyhydroxides and/or organic matter, but also through Cu leaching and migration below the topsoil horizon, and/or uptake by plants.

The mobility of Cu in soil is pH dependant: the Cu solubility increases with decreasing pH (McBride, 1994). In our case, the C-ZVI-treated soil had neutral pH and, as an earlier study at the same site showed, the treatment effectively reduced the Cu concentration in the pore water effluent by one order of magnitude (Bes and Mench, 2008). In addition, the Fe oxyhydroxide bound Cu fraction considerably increased from 22% to 50% in the treated soil (Fig. 1). Iron-containing amendments have often been applied to contaminated soils to reduce As mobility (Cundy et al., 2008; Hartley and Lepp, 2008; Kumpiene et al., 2006; Mench et al., 2003). But these amendments were not always shown to successfully immobilize Cu, usually as a result of acidification caused by certain Fe compounds, e.g. Fe-sulphates (Hartley et al., 2004), or large amount of added Fe oxides (Kumpiene et al., 2009). Due to the amphoteric nature of Fe oxides, their efficiency to sorb positively charged metals decreases with decreasing pH (Cornell and Schwertmann, 2003); hence maintaining neutral soil pH was favorable for Cu sorption to Fe oxyhydroxides.

Neutral soil pH can also favor Cu-carbonate formation. This fraction was most likely incorporated into the fraction I extracted at pH 4.5, which is below the pH value used to dissolve carbonates (e.g. Tessier et al., 1979). However, Cu concentration in fraction I of treated soil was substantially smaller than that in untreated soil indicating that Cu bound to carbonates, if present, was considerably less important than Cu bound to Fe oxides.

Copper ions have a high affinity for organic matter (e.g. Impellitteri et al., 2002; Strawn and Baker, 2009) and, as it was anticipated, OM-bound Cu fraction increased in the treated soil (Fig. 1). Nevertheless, Cu–C–O complexes were identified by EXAFS

analysis in untreated, rather than in compost/iron treated soil despite that the OM-bound Cu was the second smallest fraction in untreated soil (3.3% of total Cu, Fig. 1). The sequential extraction showed that Cu in untreated soil was predominantly in the exchangeable fraction. This fraction is extracted with ammonium-acetate, which is used to estimate all exchangeable cations in soil, including those non-specifically bound to clay minerals and organic matter (Dold, 2003; Du Laing, 2010). This fraction may also contain soluble Cu-OM complexes that are the predominant forms of dissolved Cu in soil (Sauvé et al., 1997). The EXAFS evidence for Cu(II)-organic complexes in the untreated soil suggests that a relatively large portion of the observed exchangeable fraction may be bound in soluble Cu(II)-organic complexes.

The total OM amount in compost/iron amended soil was lower than expected (5 wt% compost caused an insignificant increase in organic carbon content from $1.51 \pm 0.05\%$ to $1.92 \pm 0.37\%$), which partly could be due to the natural variability in sample composition in field experiments, but also due to the leaching of dissolved OM. Easily degradable and low molecular weight organic compounds within the compost was likely mobilized as a result of dissolution during the two years following amendment addition.

The Cu concentration in *A. castellana* shoots grown in the C-ZVI treated soil was four times lower than in the shoots from the untreated soil (Table 2). The increased species richness and greater plant biomass in the treated soil, however, resulted in the extraction of more Cu from the treated plot relative to the untreated plot. Consequently, the loss of both the exchangeable Cu and OM from soil could be partly attributed to the formation of soluble Cu-OM (e.g. fulvic acids) complexes (Impellitteri et al., 2002), their subsequent uptake by roots, Cu storage in root systems, and partial translocation to shoots (Stjernman Forsberg et al., 2009). Nevertheless, plant uptake during the two years of observation does not significantly reduce total Cu in either soil plot.

The relatively small increase in the amount of organic carbon (OC) in C-ZVI-treated soil (Table 1) caused the shift to Fe dominance where the Fe/OC ratio changed from 0.66 in the untreated soil to 1.6 in the treated soil. Under these conditions, Fe oxides, primarily poorly crystalline Fe oxyhydroxides, were responsible for Cu immobilization in C-ZVI-treated soil as confirmed by both methods of analysis, i.e. the sequential extraction and EXAFS. Hence, the EXAFS spectroscopic results provided direct evidence that the treatment successfully increased the fraction of more chemically stable Cu species bound to Fe oxyhydroxides in the soil. Since Fe-bound Cu prevails in the treated soil, Cu stability becomes sensitive to redox changes. Reductive dissolution of Fe oxides and oxyhydroxides can lead to a consequent release of bound Cu. If sulfur is present in the deeper soil horizons, Cu may readily form sulfides in reducing conditions and remain stable.

Both methods of analysis, i.e. chemical extraction and solid-state analyses, have limitations. Fractions defined by chemical extraction are operationally defined. The extraction procedure can displace a variety of compounds and cause chemical alterations in element speciation (Scheckel et al., 2003). Also, such methods are sensitive to particle loss during sample handling. These limitations can be managed by applying non-destructive solid-state analyses, such as X-ray absorption spectroscopy, although the applicability of these methods is highly system dependent. A combination of complementary analytical techniques can therefore present more reliable outcomes when predicting the long-term efficacy of in situ soil treatments.

5. Conclusions

The incorporation of compost and zerovalent iron grit (C-ZVI) into the Cu contaminated soil has changed Cu fractionation and

coordination environment in soil. Two years after the start of the aided phytostabilization experiment, the exchangeable and the most labile Cu fraction significantly decreased causing stronger-bound Cu forms to prevail in the treated soil.

The Cu(II)–C–O structure was identified as the dominant coordination environment in the untreated soil by EXAFS. Compost addition had little effect on the amount of organic carbon in the treated soil two years later. Fe oxyhydroxides became the dominant sorptive sites for Cu in the C-ZVI treated soil. The sequential extraction results coincided well with the EXAFS results. According to both methods of analysis, the dominant Cu form in treated soil was that bound to poorly crystalline Fe oxyhydroxides forming binuclear inner-sphere complexes. Prevalence of Fe-bound Cu makes the Cu stability in treated soil sensitive to seasonal variations in redox gradients, which may cause reductive dissolution of Fe oxyhydroxides and consequent mobilization of bound Cu. The coarse sandy texture of the soil as well as good drainage at the studied site may ensure the dominance of oxic conditions and Cu stability in treated soil.

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